Bifunctional Anchors Connecting Graphene Sheets and Carbon Nanotubes to Metal Electrodes for Improved Nanoelectronics

Wei-Qiao Deng, Yuki Matsuda, and William A Goddard III

Materials and Process Simulation Center, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena. CA, 91125, USA

This support information includes these sections:

Section S1 describes the computation and theoretical methodologies;

Section S2 describes detailed computation results;

Section S3 comparison with recent devices

Section S1. Theoretical Methodology

S1.1 DFT calculation:

We used the CASTEP QM code to calculate the binding energy between graphene and Pt surface connected by various anchors. We used a periodic slab with three layers of platinum atoms (12 total) to describe the Pt (111) surface. The unit cell c parameter (z direction) was at 18Å so that 50% of the unit cell is vacuum in order to avoid interactions between slabs. The calculations used the PBE nonlocal density functional theory (DFT) with the generalized gradient approximation (GGA-II) and periodic boundary conditions. [Perdew, J.P. and Y. Wang, Phys. Rev. B 1992, 46, 6671.] We used the ultrasoft plane wave pseudopotentials generated with the optimization scheme of Lin et al. [Lin, J. S.; Qteish, A.; Payne, M. C.; and Heine, V. Phys. Rev. B 1993, 47, 4174]. We found that a cutoff of 380 eV and a k-point sampling of 2x2x1 were sufficient for convergence. All energies were extrapolated to 0 K using the correction technique of Gillan and De Vita [De Vita, A.; and Gillan, M. J. J. Phys.: Condens. Matter 1991. 3, 6225]. All calculations were performed with the CASTEP code in the CERIUS2 software package. [CASTEP module: Accelrys Inc Cerius2 Modeling Environment, Release 4.0; Accelrys Inc.: San Diego, 1999.]

S1.2 IV calculation

Generally the current through molecules is expressed as;

$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V)[\, f_1(E,V_1) - f_2(E,V_2)]dE \quad (1)$$

where f_i is the Fermi-Dirac function for a voltage Vi at electrode i (1 or 2). The transmission function, T(E,V), is the sum of transmission probabilities of all channels available at energy E and is obtained through the Green function of the molecule, G_M, as affected by the electrode contacts.

$$T(E,V) = Trace[\Gamma_1(V) G_M(E,V) \Gamma_2(V) G_M^{+}(E,V)] \quad (2)$$

where Γ_i describes the coupling at electrode i.

The Green function of the molecule in equation (2), G_M, is calculated from the molecular Hamiltonian, $H_{MM}(V)$, i.e.,

$$G(E) = \begin{bmatrix} g_1^{-1} & -\tau_1 & 0 \\ -\tau_1^{+} & ES_{MM} - H_{MM} & -\tau_2^{+} \\ 0 & -\tau_2 & g_2^{-1} \end{bmatrix} = \begin{bmatrix} G_1 & G_{1M} & G_{12} \\ G_{M1} & G_{MM} & G_{2M} \\ G_{21} & G_{M2} & G_2 \end{bmatrix} \quad (3)$$

The submatrices G and g represent Green functions when interactions among subsystems are included or excluded, respectively. g_i represents the electrodes and τ_i describe the metal-molecule coupling. H_{MM} and S_{MM} are the Fock and Overlap matrices of the isolated molecule, respectively and E is the electron energy. Therefore, solving eq. 3 for G_M, we obtain

$$G_M = [ES_{MM} - H_{MM} - \Sigma_1 - \Sigma_2]^{-1} \quad (4)$$

where

$$\Sigma_1 = \tau_1^{+} g_1 \tau_1 \quad \text{and} \quad \Sigma_2 = \tau_2^{+} g_2 \tau_2 \quad (5)$$

where Σ_i are the self-energy terms coupling between the molecule and the electrodes.

All the needed parameters can be obtained from the Fock and Overlap matrices based on DFT calculations.

$$F = \begin{bmatrix} H_{11} & H_{1M} & H_{12} \\ H_{M1} & H_{MM} & H_{M2} \\ H_{21} & H_{2M} & H_{22} \end{bmatrix} \quad \text{and} \quad S = \begin{bmatrix} S_{11} & S_{1M} & S_{12} \\ S_{M1} & S_{MM} & S_{M2} \\ S_{21} & S_{2M} & S_{22} \end{bmatrix} \quad (6)$$

The metal-molecule coupling term τ_i can be determined by

$$\tau_1 = ES_{M1} - H_{M1} \quad \text{and} \quad \tau_2 = ES_{M2} - H_{M2} \quad (7)$$

H_{Mi} are the coupling matrix element between electrode and molecules.

The coupling G_i appearing in eq. 2 is given by

$$\Gamma_1 = i[\Sigma_1 - \Sigma_1^{+}] \quad \text{and} \quad \Gamma_2 = i[\Sigma_2 - \Sigma_2^{+}] \quad (8)$$

g_i are the surface green function of the electrode. For Pt, we use three layers Pt 111 slab to calculate the surface Green's function. This calculation has been implemented in SeqQuest code. See reference 19,20 in text for more details.

Section S2. Detailed calculation results

S2.1 Anchor energies

Table S3. Detailed calculation the energy of optimized slab structure (unit: eV).

	no-anchor	S linker	O linker	N linker	SO3	COO linker	CON linker
Pt surface	-8664.333	-8664.2002	-8664.303	-8664.002	-8664.361	-8664.361	-8664.263
graphene+ anchor	-1240.847	-1516.5370	-1677.158	-1511.547	-2832.737	-2270.971	-2102.563
Pt+anchor+ graphene	-9905.279	-10187.0057	-10342.153	-10178.234	-11498.884	-10937.516	-10770.608
Anchor energy (Pt-Anchor)	-0.099	-6.2684	-0.692	-2.685	-1.785	-2.184	-3.782
Pt+anchor		-8946.1463	-9100.227	-8933.128	-10258.551	-9695.874	-9528.904
Graphene		-1240.8591	-1239.707	-1238.604	-1239.963	-1239.802	-1239.816
Anchor energy (C-anchor)		-0.0002	-2.219	-6.502	-0.370	-1.841	-1.887

S2.2 Anchor structures

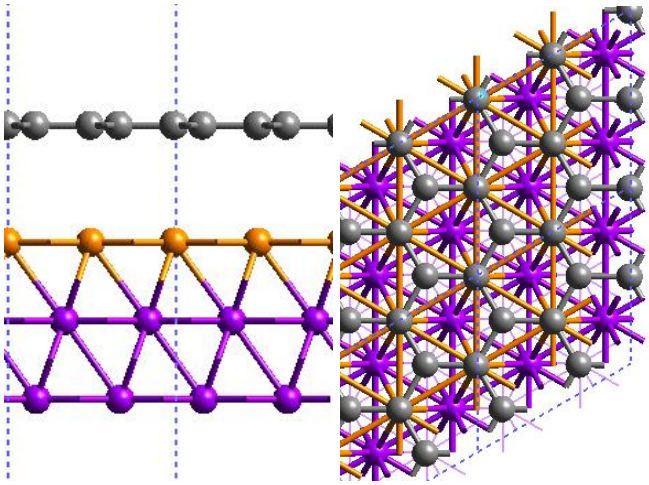

Figure S5. Optimized structure of graphene on Pt 111 surface.

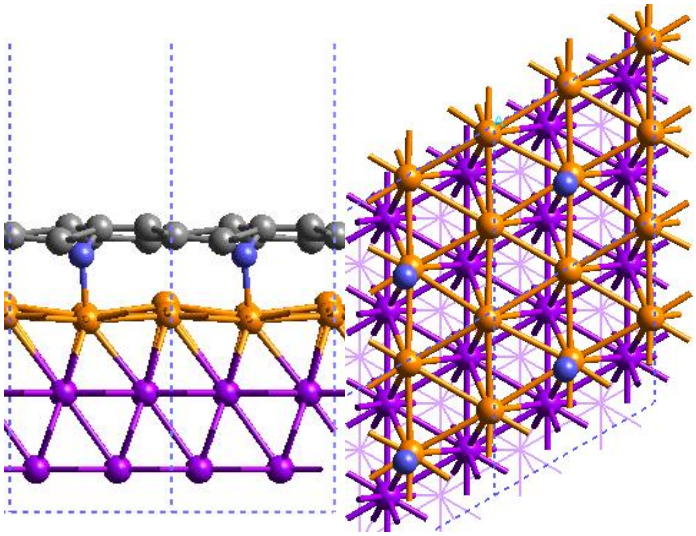

Figure S6. Optimized structures of graphene linked with Pt 111 surface by –N– anchor.

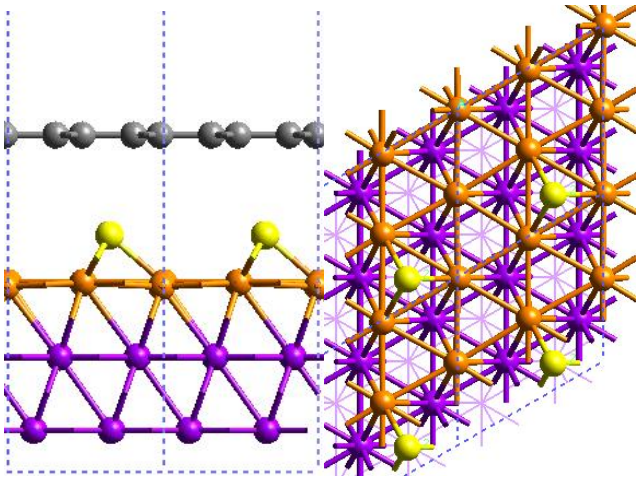

Figure S7. Optimized structure of graphene linked with Pt 111 surface by –S– anchor

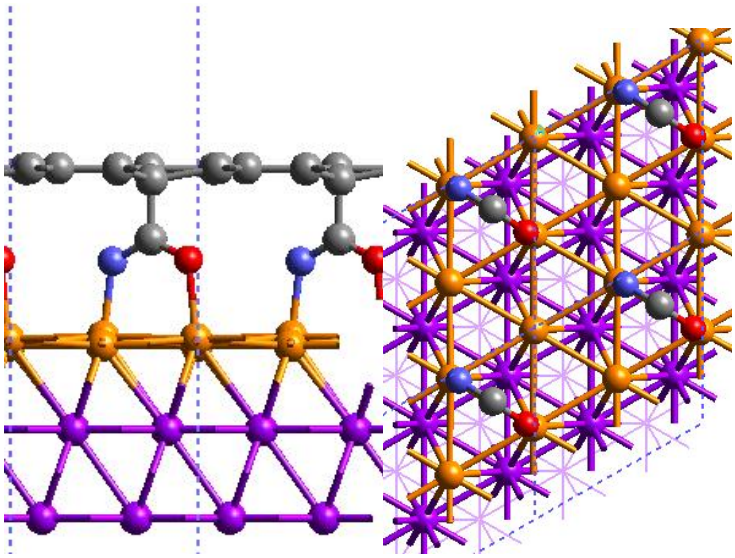

Figure S8. Optimized structure of graphene linked with Pt 111 surface by –CON– anchor

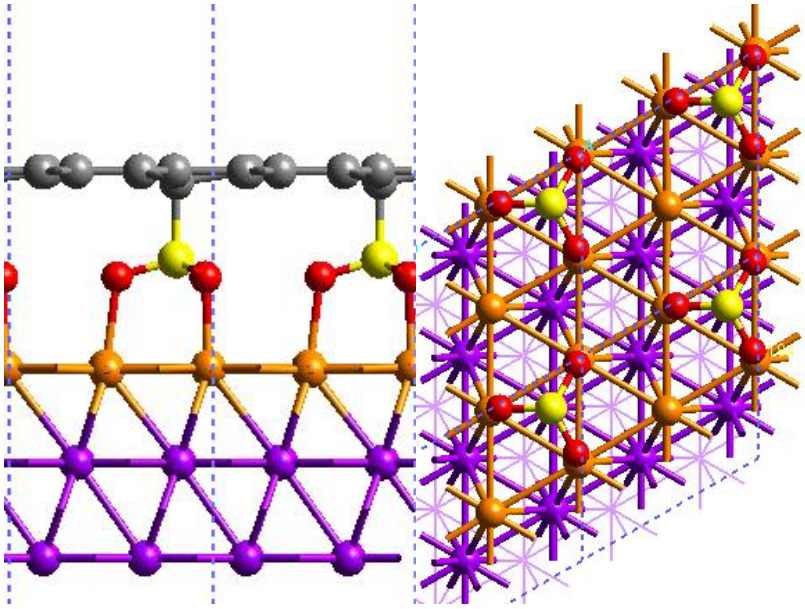

Figure S9. Optimized structure of graphene linked with Pt 111 surface by –SO3– anchor

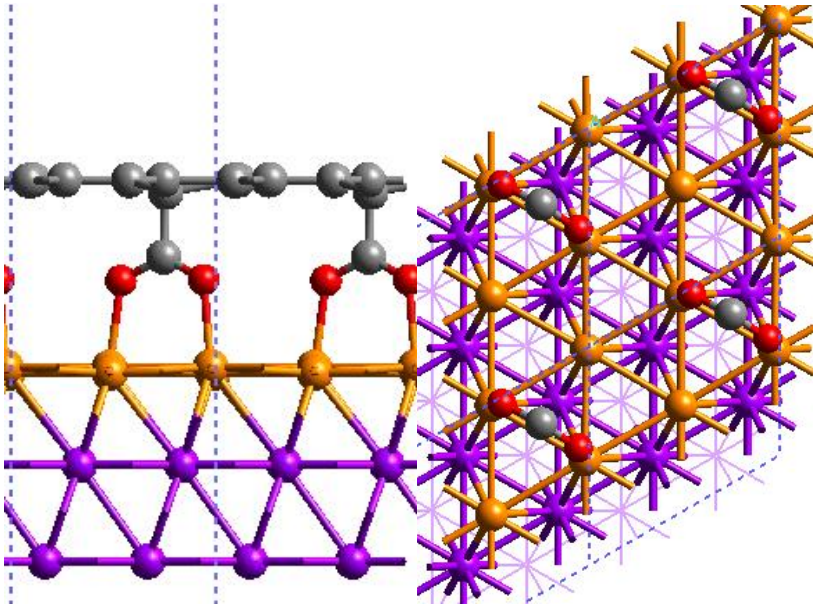

Figure S10. Optimized structure of graphene linked with Pt 111 surface by –COO– anchor

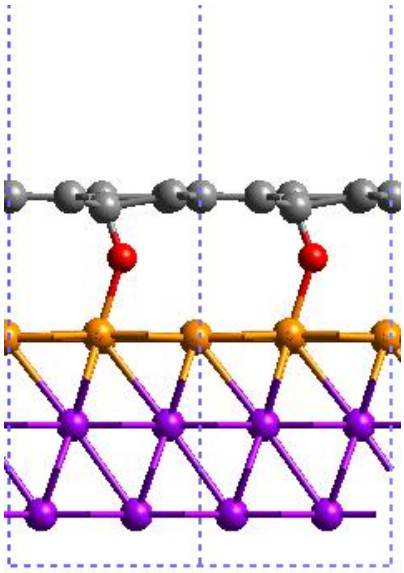

Figure S11. Optimized structure of graphene linked with Pt 111 surface by –O– anchor

S2.3 Calculated electron transport properties

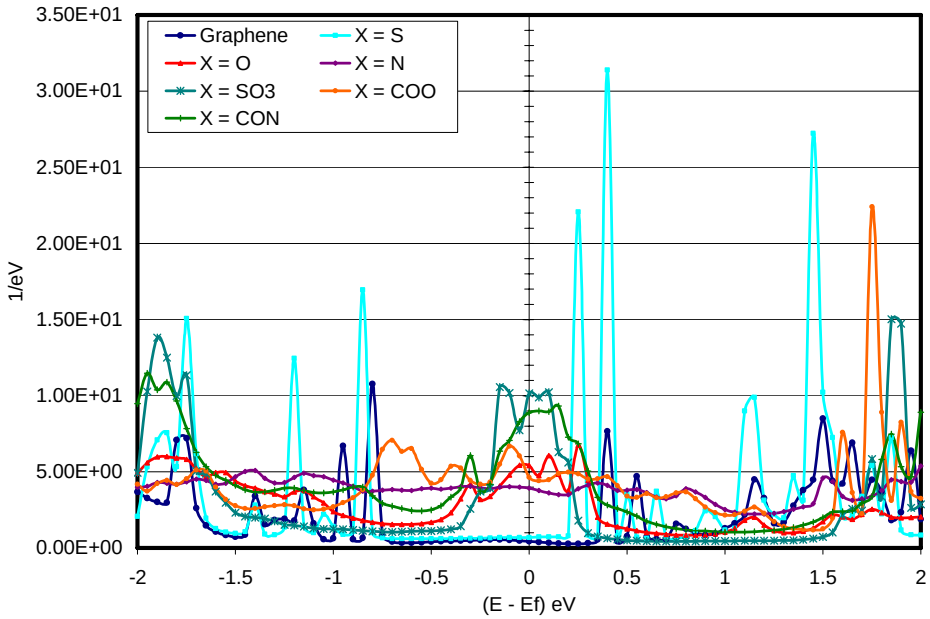

Figure S14. Density of State of the sandwich structured device.

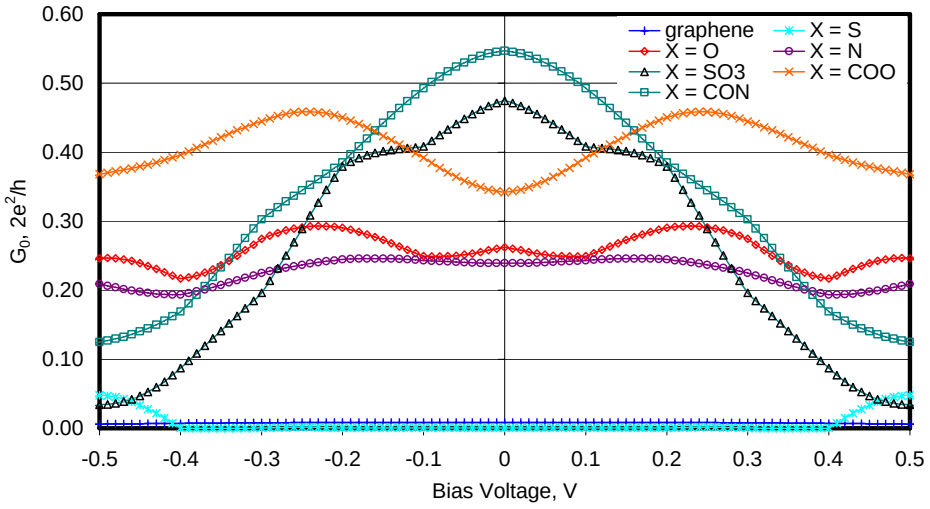

Figure S15. Electric conductivities of the sandwich structured device.

Section S3. Comparison with recent devices.

Our paper proposes the concept of anchoring graphene or carbon nanotube to metal contact in order to improve both mechanical and electrical properties. This is illustrated in Fig. S16. Recently Jeroen van den Brink has proposed a somewhat similar concept: "Graphene: From strength to strength" (Nature Nanotechnology 2, 199 – 201, 2007) doi:10.1038/nnano.2007.91). This is illustrated in Figure S17.

The comparison between our propose concept and current demonstrated device.

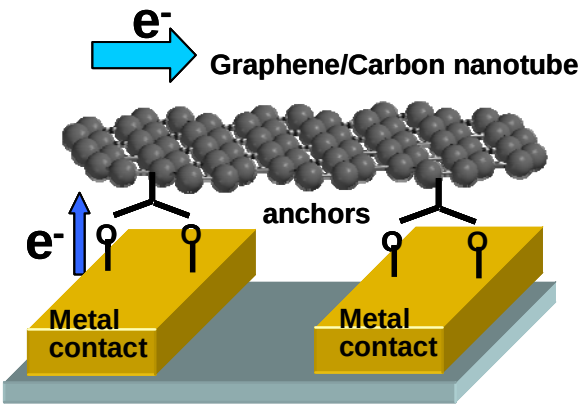

Figure S16. Our concept

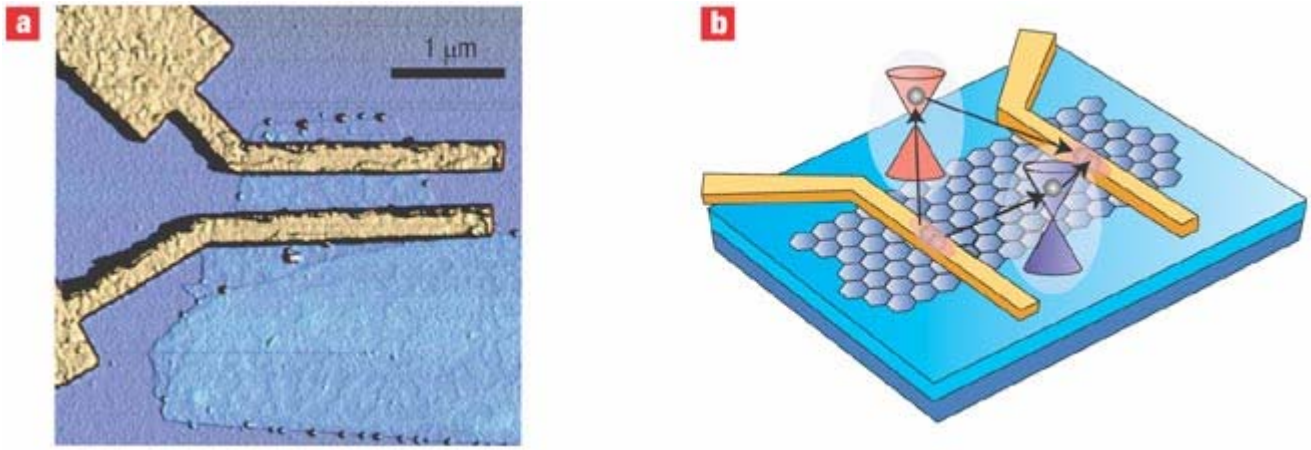

Figure S17. The concept of a graphene transistor (from van den Brink).